Hyperfine interaction and Knight shift
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The **Knight shift** is a shift in the nuclear magnetic resonance frequency of a paramagnetic substance first published in 1949 by the American physicist Walter David Knight. The Knight shift refers to the relative shift K in NMR frequency for atoms in a metal (e.g. sodium) compared with the same atoms in a nonmetallic environment (e.g. sodium chloride). The observed shift reflects the local magnetic field produced at the sodium nucleus by the magnetization of the conduction electrons. The average local field in sodium augments the applied resonance field by approximately one part per 1000. In nonmetallic sodium chloride the local field is negligible in comparison.

The Knight shift is due to the conduction electrons in metals. They introduce an "extra" effective field at the nuclear site, due to the spin orientations of the conduction electrons in the presence of an external field. This is responsible for the shift observed in the nuclear magnetic resonance. The shift comes from two sources, one is the Pauli paramagnetic spin susceptibility, the other is the s-component wave functions at the nucleus. Depending on the electronic structure, the Knight shift may be temperature dependent. However, in metals which normally have a broad featureless electronic density of states, Knight shifts are temperature independent.

http://en.wikipedia.org/wiki/Knight_shift

1.   Introduction

There is an interaction between the magnetic moment of a nucleus and the magnetic moment of electron (orbital magnetic moment and spin magnetic moment). This interaction is very important in the nuclear magnetic resonance (NMR). Through this interaction, the information on the properties of electrons surrounding the nucleus can be observed by NMR. The interaction consists of the dipole-dipole interaction (spin-dipolar interaction), the hyperfine interaction (Fermi contact field), and the crystal field (related to the orbital angular momentum).

2.   The coupling Hamiltonian between electron and nucleus (Abraham)
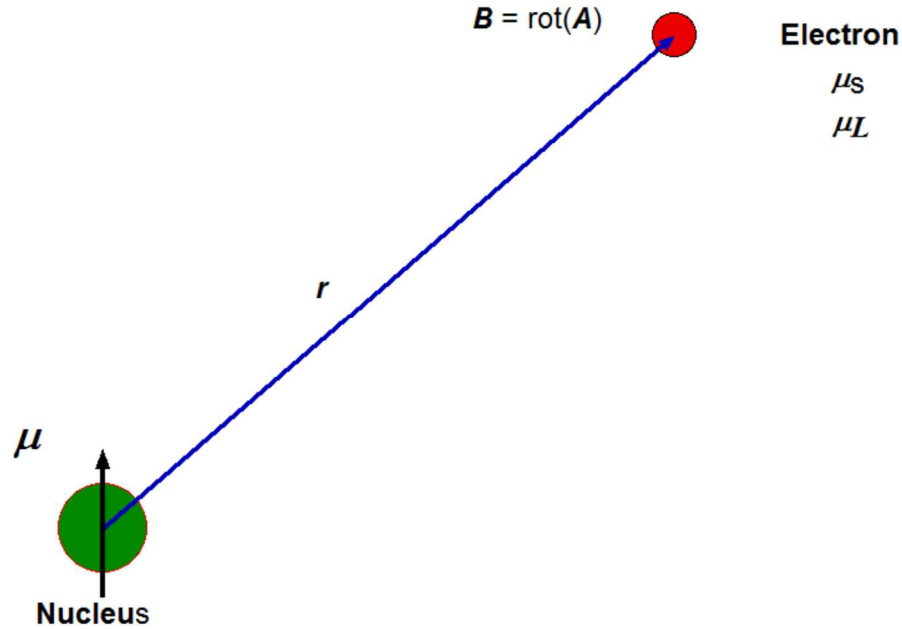
The behavior of an electron [$q = -e$ (charge of electron); m (mass of electron)] in a magnetic field $\boldsymbol{B}$ produced by a nucleus, is given by the Hamiltonian

$$H = \frac{1}{2m}(\boldsymbol{p} - \frac{q}{c}\boldsymbol{A})^2 - (-2\mu_B \boldsymbol{s}) \cdot \boldsymbol{B}.$$

where μ_B is the Bohr magneton of electron

$$\mu_B = \frac{e\hbar}{2mc}.$$

$\boldsymbol{s} = \boldsymbol{S}/\hbar$ and $\boldsymbol{S}$ is the spin angular momentum (in the units of $\hbar$). The second term arises from the spin magnetic moment in the presence of magnetic field $\boldsymbol{B}$. According to the classical electromagnetic theory, the magnetic moment of nucleus $(\boldsymbol{\mu} = \gamma\hbar\boldsymbol{I})$ produces at a point removed from it by a vector $\boldsymbol{r}$, a magnetic field $\boldsymbol{B}$

$$\boldsymbol{B} = \nabla \times \boldsymbol{A},$$

with

$$\boldsymbol{A} = \boldsymbol{\mu} \times \frac{\boldsymbol{r}}{r^3},$$

where $\boldsymbol{A}$ is the magnetic vector potential. Noting that

$$\nabla \frac{1}{r} = -\frac{\mathbf{r}}{r^3} .$$

Then we get

$$\mathbf{B} = \nabla \times \mathbf{A} = \nabla \times (\boldsymbol{\mu} \times \frac{\mathbf{r}}{r^3}) = -\nabla \times [\boldsymbol{\mu} \times \nabla \frac{1}{r}] = \nabla \times [\nabla \times (\frac{\boldsymbol{\mu}}{r})] ,$$

since

$$\nabla \times \left(\frac{\boldsymbol{\mu}}{r}\right) = \nabla \frac{1}{r} \times \boldsymbol{\mu} + \frac{1}{r} \nabla \times \boldsymbol{\mu} = \nabla \frac{1}{r} \times \boldsymbol{\mu} = -\boldsymbol{\mu} \times \nabla \frac{1}{r} .$$

(b)   The vector A satisfies the Coulomb gauge,

$$\nabla \cdot \mathbf{A} = 0 .$$

since

$$\nabla \cdot \mathbf{A} = \nabla \cdot (\boldsymbol{\mu} \times \frac{\mathbf{r}}{r^3})$$

$$= \frac{\mathbf{r}}{r^3} \cdot (\nabla \times \boldsymbol{\mu}) - \boldsymbol{\mu} \cdot (\nabla \times \frac{\mathbf{r}}{r^3}) = 0$$

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```
Clear["Global`*"];

Needs["VectorAnalysis`"]; SetCoordinates[Cartesian[x, y, z]];

μ = {μ1, μ2, μ3}; r = √(x² + y² + z²) ; R = {x, y, z}; R1 = R / r³;

A1 = Cross[μ, R1] // Simplify
```

$$\left\{ \frac{z\,\mu 2 - y\,\mu 3}{\left(x^2 + y^2 + z^2\right)^{3/2}}, \frac{-z\,\mu 1 + x\,\mu 3}{\left(x^2 + y^2 + z^2\right)^{3/2}}, \frac{y\,\mu 1 - x\,\mu 2}{\left(x^2 + y^2 + z^2\right)^{3/2}} \right\}$$

```
Div[A1] // FullSimplify
```

0

```
Curl[R1] // FullSimplify
```

{0, 0, 0}

```
B1 = Curl[A1] // FullSimplify
```

$$\left\{ \frac{2\,x^2\,\mu 1 - \left(y^2 + z^2\right)\mu 1 + 3\,x\,(y\,\mu 2 + z\,\mu 3)}{\left(x^2 + y^2 + z^2\right)^{5/2}}, \right.$$

$$\frac{3\,x\,y\,\mu 1 - x^2\,\mu 2 + 2\,y^2\,\mu 2 - z^2\,\mu 2 + 3\,y\,z\,\mu 3}{\left(x^2 + y^2 + z^2\right)^{5/2}}, \left. \frac{3\,z\,(x\,\mu 1 + y\,\mu 2) - \left(x^2 + y^2 - 2\,z^2\right)\mu 3}{\left(x^2 + y^2 + z^2\right)^{5/2}} \right\}$$

Near the origin, *A* has a singularity of order r^{-2} and *B* has a singularity of order r^{-3}, so some care must be exerted in the calculation of its interaction.

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3. Magnetic field ditribution due to the magnetic moment of nucleus

Suppose that the magnetic moment of the nucleus is directed along the z axis at the origin.

$$\boldsymbol{\mu} = (0,0,\mu_0), \qquad \mathbf{A} = \boldsymbol{\mu} \times \frac{\mathbf{r}}{r^3}$$

The magnetic field produced by the magnetic mpoment of nucleus is

$$\boldsymbol{B} = \nabla \times \boldsymbol{A} = \frac{\mu_0}{r^5}\left(zx, yz, x^2 + y^2 - 2z^2\right)$$

We make a plot of *B* in the *y-z* plane by using the StreamPlot (Mathyematica), where μ_0 = 1.

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((Mathematica))

```
Clear["Gobal`"]

Needs["VectorAnalysis`"]

SetCoordinates[Cartesian[x, y, z]]
```

Cartesian[x, y, z]

```
r = {x, y, z}; m = {0, 0, m0};
```

$$A = \frac{1}{(r.r)^{3/2}} \; Cross[m, r] \; // \; Simplify$$

$$\left\{ -\frac{m0\; y}{\left(x^2 + y^2 + z^2\right)^{3/2}}, \; \frac{m0\; x}{\left(x^2 + y^2 + z^2\right)^{3/2}}, \; 0 \right\}$$

```
B = Curl[A] // Simplify
```

$$\left\{ \frac{3\, m0\; x\; z}{\left(x^2 + y^2 + z^2\right)^{5/2}}, \; \frac{3\, m0\; y\; z}{\left(x^2 + y^2 + z^2\right)^{5/2}}, \; -\frac{m0\, \left(x^2 + y^2 - 2\, z^2\right)}{\left(x^2 + y^2 + z^2\right)^{5/2}} \right\}$$

```
rule1 = {m0 → 1, x → 0};

B1 = B /. rule1
```

$$\left\{ 0, \; \frac{3\, y\; z}{\left(y^2 + z^2\right)^{5/2}}, \; -\frac{y^2 - 2\, z^2}{\left(y^2 + z^2\right)^{5/2}} \right\}$$

```
f1 = StreamPlot[{B1[[2]], B1[[3]]}, {y, -3, 3}, {z, 3, -3},
    StreamStyle → Purple];

f2 = Graphics[{Red, Thick, Arrow[{{0, -0.5}, {0, 0.5}}],
    Black, Thin, Line[{{-3, 0}, {3, 0}}],
    Line[{{0, -3}, {0, 3}}],
    Text[Style["y", Black, 12], {3.2, 0}],
    Text[Style["z", Black, 12], {0, 3.2}] }];

Show[f1, f2]
```
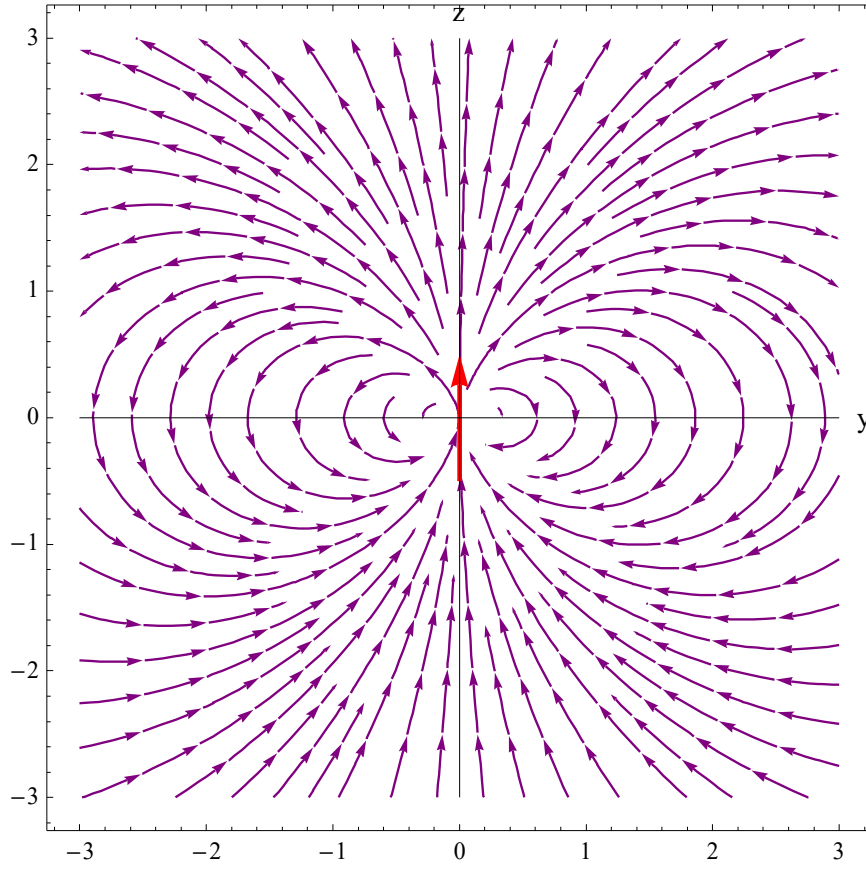
Fig.   The distribution of the magnetic field $\boldsymbol{B}$ produced by the magnetic moment of nucleus at the origin (along the z axis) in the *y-z* plane.

4.   Orbital magnetic moment contribution

The Hamiltonian arising from the orbitral motion of the electron isgiven by

$$
\begin{aligned}
H_L &= \frac{1}{2m}(\boldsymbol{p}-\frac{q}{c}\boldsymbol{A})^2 \\
&= \frac{1}{2m}(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A})\cdot(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A}) \\
&= \frac{1}{2m}[\boldsymbol{p}^2+\frac{e}{c}(\boldsymbol{p}\cdot\boldsymbol{A}+\boldsymbol{A}\cdot\boldsymbol{p})]+\frac{e^2}{2mc^2}\boldsymbol{A}^2 \\
&= H_0+H_L{}'
\end{aligned}
$$

with

$$
H_0 = \frac{1}{2m}\boldsymbol{p}^2,
$$

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and

$$H_L' = \frac{e}{2mc}(\boldsymbol{p} \cdot \boldsymbol{A} + \boldsymbol{A} \cdot \boldsymbol{p}) + \frac{e^2}{2mc^2}\boldsymbol{A}^2 .$$

In the first order (the order of A) perturbation , we have

$$H_L' = \frac{e}{2mc}(\boldsymbol{p} \cdot \boldsymbol{A} + \boldsymbol{A} \cdot \boldsymbol{p}) = \frac{\mu_B}{\hbar}(\boldsymbol{p} \cdot \boldsymbol{A} + \boldsymbol{A} \cdot \boldsymbol{p})] .$$

Here we calculate

$$H_L' \psi(\boldsymbol{r}) = \frac{\mu_B}{\hbar}(\boldsymbol{p} \cdot \boldsymbol{A} + \boldsymbol{A} \cdot \boldsymbol{p})]\psi(\boldsymbol{r}) .$$

where $\psi(\boldsymbol{r})$ is an arbitrary wave function and $\boldsymbol{p}$ is the quantum mechanical operator defined by

$$\boldsymbol{p} = \frac{\hbar}{i}\nabla .$$

Using the formula (vector analysis),

$$\nabla \cdot (\boldsymbol{A}\psi(\boldsymbol{r})) = \boldsymbol{A} \cdot \nabla \psi(\boldsymbol{r}) + \psi(\boldsymbol{r})\nabla \cdot \boldsymbol{A},$$

we get

$$\begin{aligned}
H_L' \psi(\boldsymbol{r}) &= \frac{\mu_B}{i}[\psi(\boldsymbol{r})\nabla \cdot \boldsymbol{A} + 2\boldsymbol{A} \cdot \nabla \psi(\boldsymbol{r})] \\
&= \frac{2\mu_B}{i}\boldsymbol{A} \cdot \nabla \psi(\boldsymbol{r}) \\
&= \frac{2\mu_B}{\hbar}(\boldsymbol{\mu} \times \frac{\boldsymbol{r}}{r^3}) \cdot \boldsymbol{p}\psi(\boldsymbol{r}) \\
&= \frac{2\mu_B}{\hbar}(\frac{\boldsymbol{r} \times \boldsymbol{p}}{r^3}) \cdot \boldsymbol{\mu}\psi(\boldsymbol{r}) \\
&= \frac{2\mu_B}{r^3}\frac{\boldsymbol{L}}{\hbar} \cdot \boldsymbol{\mu}\psi(\boldsymbol{r}) = \frac{2\mu_B}{r^3}\boldsymbol{l} \cdot \boldsymbol{\mu}\psi(\boldsymbol{r})
\end{aligned}$$

wehere we use $\nabla \cdot \boldsymbol{A} = 0$ and

$$A = \mu \times \frac{r}{r^3}$$

The orbital angular momentum L is defined as

$$L = \hbar l = r \times p .$$

in the quantum mechanics. Then the Hamiltonian can be written as

$$H_L' = 2\mu_B \frac{l \cdot \mu}{r^3}$$

We note that the orbital magnetic moment μ_L is

$$\mu_L = -\frac{\mu_B}{\hbar} L = -\mu_B l .$$

5.   Spin magnetic moment contribution

The interaction between the spin magnetic moment of electron and μ is

$$H_S' = -(-2\mu_B s) \cdot B$$
$$= 2\mu_B s \cdot [\nabla \times [\nabla \times \frac{\mu}{r}]]$$
$$= 2\mu_B s \cdot [\nabla(\nabla \cdot \frac{\mu}{r}) - \nabla^2 \frac{\mu}{r}]$$

where the spin magnetic moment is given by

$$\mu_S = (-2\mu_B s) = -\frac{2\mu_B}{\hbar} S .$$

and S is the spin angular momentum (in the units of $\hbar$). Here we use the formula

$$\nabla \times (\nabla \times F) = \nabla(\nabla \cdot F) - \nabla^2 F$$

where F is any vector. We note that

$$\nabla \cdot \frac{\boldsymbol{\mu}}{r} = \boldsymbol{\mu} \cdot \nabla \frac{1}{r} + \frac{1}{r} \nabla \cdot \boldsymbol{\mu} = \boldsymbol{\mu} \cdot \nabla \frac{1}{r}$$

where $\boldsymbol{\mu}$ is independent of $\boldsymbol{r}$. Then we have

$$\nabla(\nabla \cdot \frac{\boldsymbol{\mu}}{r}) = \nabla(\boldsymbol{\mu} \cdot \nabla \frac{1}{r}) = (\boldsymbol{\mu} \cdot \nabla)\nabla \frac{1}{r} + \boldsymbol{\mu} \times (\nabla \times \nabla\left(\frac{1}{r}\right)) = (\boldsymbol{\mu} \cdot \nabla)\nabla \frac{1}{r}$$

$$\nabla^2 \frac{\boldsymbol{\mu}}{r} = \boldsymbol{\mu}\nabla^2 \frac{1}{r}$$

The interaction H_S' can be written as

$$H_S' = 2\mu_B \boldsymbol{s} \cdot [(\boldsymbol{\mu} \cdot \nabla)\nabla(\frac{1}{r}) - \boldsymbol{\mu}\nabla^2(\frac{1}{r})]$$

$$= 2\mu_B[(\boldsymbol{\mu} \cdot \nabla)(\boldsymbol{s} \cdot \nabla) - (\boldsymbol{s} \cdot \boldsymbol{\mu})\nabla^2](\frac{1}{r})$$

This can be rewritten as

$$H_S' = 2\mu_B[(\boldsymbol{\mu} \cdot \nabla)(\boldsymbol{s} \cdot \nabla) - (\boldsymbol{s} \cdot \boldsymbol{\mu})\nabla^2](\frac{1}{r})$$

Here we notice that for $r \neq 0$

$$(\boldsymbol{\mu} \cdot \nabla)(\boldsymbol{s} \cdot \nabla)(\frac{1}{r}) = \frac{-(\boldsymbol{\mu} \cdot \boldsymbol{s})r^2 + 3(\boldsymbol{\mu} \cdot \boldsymbol{r})(\boldsymbol{s} \cdot \boldsymbol{r})}{r^5}$$

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```mathematica
Clear["Global`*"]; Needs["VectorAnalysis`"];
SetCoordinates[Cartesian[x, y, z]]; s = {s1, s2, s3}; μ = {μ1, μ2, μ3};
r = √(x² + y² + z²) ;
R = {x, y, z};

L1[a_] := (a[[1]] D[#, x] + a[[2]] D[#, y] + a[[3]] D[#, z]) &;

f1 = L1[μ][L1[s][1 / r]] // FullSimplify
```

$$\frac{1}{\left(x^2 + y^2 + z^2\right)^{5/2}} \left(3\, s3\, z\, (x\, \mu1 + y\, \mu2) - \right.$$
$$s3\, \left(x^2 + y^2 - 2\, z^2\right) \mu3 + s2\, \left(3\, x\, y\, \mu1 - x^2\, \mu2 + 2\, y^2\, \mu2 - z^2\, \mu2 + 3\, y\, z\, \mu3\right) +$$
$$\left. s1\, \left(2\, x^2\, \mu1 - \left(y^2 + z^2\right) \mu1 + 3\, x\, (y\, \mu2 + z\, \mu3)\right)\right)$$

```mathematica
f2 = 1/r⁵ (3 (μ.R) (s.R) - (μ.s) r²) // FullSimplify
```

$$\frac{-\left(x^2 + y^2 + z^2\right) (s1\, \mu1 + s2\, \mu2 + s3\, \mu3) + 3\, (s1\, x + s2\, y + s3\, z)\, (x\, \mu1 + y\, \mu2 + z\, \mu3)}{\left(x^2 + y^2 + z^2\right)^{5/2}}$$

```mathematica
f1 - f2 // Simplify
```

0

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6.   The expression of H_S' near the origin (White): hyperfine interaction

We start with the spin Hamilonian

$$H_S' = 2\mu_B \mathbf{s} \cdot \nabla \times \mathbf{A}(r)$$

The matrix element of the Hamiltonian for the wave function $\psi(\mathbf{r})$

$$W_m^s = \left\langle \psi \left| H_s' \right| \psi \right\rangle$$
$$= 2\mu_B \int d\mathbf{r} \, \psi^*(\mathbf{r})[\mathbf{s} \cdot \nabla \times \mathbf{A}(\mathbf{r})]\psi(\mathbf{r})$$
$$= 2\mu_B \left[\int_{r<\delta} d\mathbf{r} \, \psi^*(\mathbf{r})\mathbf{s} \cdot \nabla \times \mathbf{A}(\mathbf{r})\psi(\mathbf{r}) + \int_{r>\delta} d\mathbf{r} \, \psi^*(\mathbf{r})\mathbf{s} \cdot \nabla \times \mathbf{A}(\mathbf{r})\psi(\mathbf{r})\right]$$

where the radius δ defines a sphere which encloses the nucleus. Outside the sphere $\mathbf{A}(r)$ is given by

$$\mathbf{A} = \boldsymbol{\mu} \times \frac{\mathbf{r}}{r^3}$$

The second term in W_m^s ($W_s^{m(2)}$) gives the dipole-dipole interaction since $r > \delta$. The first term in W_m^s is the additional interaction

$$W_s^{m(1)} = 2\mu_B \int_{r<\delta} dr \psi^*(r) s \cdot \nabla \times [A(r)\psi(r)]$$

Using the vector analysis

$$\nabla \cdot [A(r)\psi(r) \times s] = s \cdot \nabla \times [A(r)\psi(r)] - A(r)\psi(r) \cdot \nabla \times s$$

we get

$$\nabla \cdot [A(r)\psi(r) \times s] = s \cdot \nabla \times [A(r)\psi(r)]$$

where we use the assumption that s is independent of r; $\nabla \times s = 0$. Then we get

$$W_s^{m(1)} = 2\mu_B \int_{r<\delta} dr |\psi(r)|^2 \nabla \cdot (A(r) \times s)$$

since

$$\nabla \cdot [(A(r) \times s)\psi(r)] = \nabla \psi(r) \cdot (A(r) \times s) + \psi(r)\nabla \cdot (A(r) \times s)$$
$$= \psi(r)\nabla \cdot (A(r) \times s)$$

Note that $\psi(r)$ is independent of r for $r<\delta$; $\psi(r) = \psi(0)$. Then we have

$$W_s^{m(1)} = 2\mu_B |\psi(0)|^2 \int_{r<\delta} dr \nabla \cdot (A(r) \times s)$$
$$= 2\mu_B |\psi(0)|^2 \int_{r<\delta} da \cdot (A(r) \times s)$$
$$= 2\mu_B |\psi(0)|^2 s \cdot \int_{r<\delta} da \times A(r)$$

We also use the Gauss's theorem. Because of the sphere of integrals has been chosen to lie outside the nucleus,

$$A(r) = \mu \times \frac{r}{r^3}$$

$$W_s^{m(1)} = 2\mu_B |\psi(0)|^2 s \cdot \int_{r<\delta} da \times (\mu \times \frac{r}{r^3}) = 2\mu_B |\psi(0)|^2 s \cdot \frac{8\pi}{3} \mu = \frac{16\pi}{3} \mu_B s \cdot \mu |\psi(0)|^2$$

Note that

$$\int_{r<\delta} d\boldsymbol{a} \times (\boldsymbol{\mu} \times \frac{\boldsymbol{r}}{r^3}) = \int r^2 d\Omega \frac{\boldsymbol{r}}{r} \times (\boldsymbol{\mu} \times \frac{\boldsymbol{r}}{r^3})$$

$$= \int d\Omega \frac{1}{r^2} [r^2 \boldsymbol{\mu} - \boldsymbol{r}(\boldsymbol{r} \cdot \boldsymbol{\mu})]$$

$$= \int d\Omega [\boldsymbol{\mu} - \frac{\boldsymbol{r}(\boldsymbol{r} \cdot \boldsymbol{\mu})}{r^2}]$$

$$= 4\pi\boldsymbol{\mu} - 2\pi\boldsymbol{\mu} \int_0^\pi \sin^3 \theta d\theta$$

$$= 4\pi\boldsymbol{\mu} - 2\pi\boldsymbol{\mu} \frac{4}{3}$$

$$= \frac{8\pi}{3} \boldsymbol{\mu}$$

where $d\boldsymbol{a}$ is the surface element normal to the surface of sphere. Note that

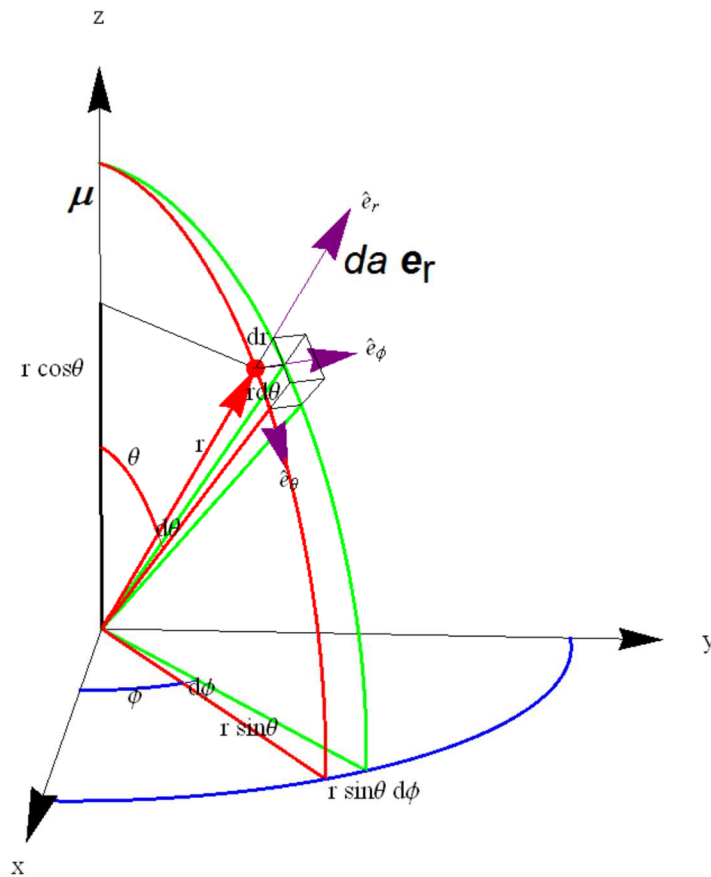$$d\boldsymbol{a} = da \boldsymbol{e}_r = r^2 d\Omega \frac{\boldsymbol{r}}{r}$$

with

$$d\Omega = \sin \theta d\theta d\phi$$

dΩ is the solid angle. For simplicity we assume that $\boldsymbol{\mu}$ is directed along the z axis.

$$\boldsymbol{\mu} - \frac{\boldsymbol{r}(\boldsymbol{r} \cdot \boldsymbol{\mu})}{r^2} = \mu \boldsymbol{e}_z - \frac{\mu r^2}{r^2} \cos \theta (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$$

$$= (0,0,\mu) - \mu(\sin \theta \cos \theta \cos \phi, \sin \theta \cos \theta \sin \phi, \cos^2 \theta)$$

$$= \mu(-\sin \theta \cos \theta \cos \phi, \sin \theta \cos \theta \sin \phi, \sin^2 \theta)$$

This is the contact hyperfine interaction

6. Magnetic hyperfine field

The resulting Hamiltonian is obtained as

$$H_1 = -2\mu_B \frac{(\boldsymbol{\mu}\cdot\boldsymbol{s})r^2 - 3(\boldsymbol{\mu}\cdot\boldsymbol{r})(\boldsymbol{s}\cdot\boldsymbol{r})}{r^5} + \frac{16}{3}\pi\mu_B(\boldsymbol{s}\cdot\boldsymbol{\mu})\delta(\boldsymbol{r}) + 2\mu_B \frac{\boldsymbol{l}\cdot\boldsymbol{\mu}}{r^3}$$

The first term is a dipole-dipole interaction and the second term is a contact term of the hyperfine interaction. Since

$$H_1 = -\boldsymbol{\mu}\cdot\boldsymbol{H}_{loc}$$

The local field $\boldsymbol{H}_{loc}$ seen by a nucleus is given by

$$H_{loc} = -2\mu_B [\frac{l}{r^3} - \frac{s}{r^3} + \frac{3r(s \cdot r)}{r^5} + \frac{8}{3}\pi s \delta(r)]$$

7.　　Knight shift in metals (White)

The s-like conductuion electrons produce a contact hyperfine field at the nuclei of a metal. Thus, if the conduction electrons are polarized by an external field, at a fixed frequency the resonance of a nuclear spin is observed at a slightly different magnetic field in a metal than in a diamagnetic solid. This effect is known as the Knight shift or metallic shift.

$$K = -\frac{<H_{loc}{}^z>}{H_0}.$$

The local field $<H_{loc}{}^z>$ is given by

$$\left\langle H_{loc}{}^z \right\rangle = -\frac{16\pi}{3}\mu_B \left\langle S_z \right\rangle \int \psi^*(r)\delta(r)\psi(r)dr = -\frac{16\pi}{3}\mu_B \left\langle S_z \right\rangle |\psi(0)|^2$$

The average conduction electron spin $\left\langle S_z \right\rangle$ is related to the Pauli spin susceptibility χ_s of the conduction electrons,

$$M_z = g\mu_B N \left\langle S_z \right\rangle = \chi_s H_0.$$

The Knight shift is rewritten as

$$K = \frac{16\pi}{3}\mu_B \frac{\chi_s}{g\mu_B N}|\psi(0)|^2 \approx \frac{\chi_s}{N}|\psi(0)|^2,$$

where

$$\frac{1}{N}|\psi(0)|^2,$$

is the ratio of the conduction electron concentration at the nucleus to the average conduction electron. The spin susceptibility can be determined by very careful conduction electron spin resonance experiment.

8.　　Pauli paramagnetism and density of states in metal

The susceptibility due to the Pauli paramagnetism of conduction electrons is obtained as.

$$\chi_s = \mu_B{}^2 D(\varepsilon_F) = 2\mu_B{}^2 N(\varepsilon_F). \tag{41}$$

For metals which is well described by free electron model, the Knight shift is proportional to the density of states at the Fermi level (per spin).

REFERENCES
W.D. Knight, *Solid State Phys*. **2**, 93 (1956).
A. Abragam, *The Principle of Nuclear Magnetism* (Oxford at the Clarendon Press)
R.M. White, *Quantum Theory of Magnetism* (Springer, Berlin, 2007)
H.J. Zeiger and G.W. Pratt, *Magnetiuc interactions in solids* (Clarendon Press, Oxford 1973).